

CIRCULATION COPY

SUBJECT TO RECALL  
IN TWO WEEKS

UCRL- 83540  
PREPRINT

THE UTILIZATION OF  $\text{ZnSO}_4$  DECOMPOSITION  
IN THERMOCHEMICAL HYDROGEN CYCLES

Oscar H. Krikorian  
Pamela K. Hosmer

This paper was prepared for submittal to  
the Third World Hydrogen Energy Conference  
Tokyo, Japan, June 23-26, 1980

February 25, 1980



Lawrence  
Livermore  
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

# THE UTILIZATION OF $\text{ZnSO}_4$ DECOMPOSITION IN THERMOCHEMICAL HYDROGEN CYCLES<sup>1</sup>

Oscar H. Krikorian and Pamela K. Hosmer

Lawrence Livermore National Laboratory,  
Livermore, CA 94550 U.S.A.

## ABSTRACT

We find that the  $\text{ZnSO}_4$  decomposition reaction can be used as the high temperature step in a number of thermochemical cycles. It is especially applicable as a substitute for the  $\text{H}_2\text{SO}_4$  decomposition step in  $\text{H}_2\text{SO}_4$ -based cycles, and significantly improves the efficiency of such cycles. In this study, we have taken an initial look at the effects of heatup rate on the decomposition of  $\text{ZnSO}_4$  as it is heated through an  $\alpha$ - $\beta$  transition at 1015 K. We find that a rapid heatup of fine  $\text{ZnSO}_4$  particulates through this transition leads to fracturing of the  $\text{ZnSO}_4$  crystallites and significantly enhances its subsequent decomposition rate at  $\sim 1043$  K. We also find evidence for an autocatalytic decomposition process in fine  $\text{ZnSO}_4$  particulates with either rapid or slow heatup rates. We believe that a combination of (1) fracturing of the crystallites and (2) surface catalysis by  $\text{ZnO}$  to equilibrate the  $\text{SO}_3/\text{SO}_2/\text{O}_2$  gaseous products, contributes to the observed autocatalytic behavior.

## INTRODUCTION

We have been conducting basic studies on the  $\text{ZnSO}_4$  decomposition reaction in order to evaluate the potential use of this reaction as the high temperature step in a number of thermochemical cycles. Our studies thus far have concentrated on determining the basic thermodynamics, kinetics and mechanism for the reaction at temperatures up to  $\sim 1200$  K where the decomposition pressure reaches a value of about one atmosphere. In this paper, we will report on some initial studies on  $\text{ZnSO}_4$  decomposition under dynamic heatup conditions, and show how the rate of heating through an  $\alpha$ - $\beta$  transition in  $\text{ZnSO}_4$  at 1015 K affects its subsequent decomposition kinetics.

The  $\text{ZnSO}_4$  decomposition reaction is the highest temperature reaction step in the ZnSe Thermochemical Cycle (Krikorian, 1978) under study at the Lawrence Livermore National Laboratory, and is given as reaction (4) below for the ZnSe Cycle which has the following steps:

---

<sup>1</sup>This study was sponsored by the U.S. Department of Energy-Office of Basic Energy Science and performed by the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

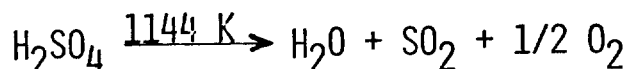
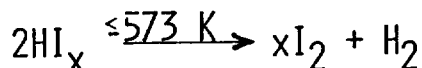
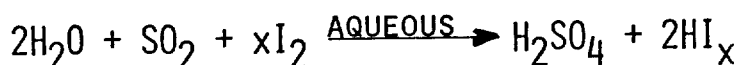
- (1)  $2\text{ZnO}(\text{s}) + \text{Se}(\text{l}) + \text{SO}_2(\text{g}) \xrightarrow{800 \text{ K}} \text{ZnSe}(\text{s}) + \text{ZnSO}_4(\text{s})$
- (2)  $\text{ZnSe}(\text{s}) + 2\text{HCl}(\text{g}) \xrightarrow{350 \text{ K}} \text{ZnCl}_2(\text{aq}) + \text{H}_2\text{Se}(\text{g})$
- (3)  $\text{ZnCl}_2(\text{l}) + \text{H}_2\text{O}(\text{g}) \xrightarrow{900 \text{ K}} \text{ZnO}(\text{s}) + 2\text{HCl}(\text{g})$
- (4)  $\text{ZnSO}_4(\text{s}) \xrightarrow{1200 \text{ K}} \text{ZnO}(\text{s}) + \text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$
- (5)  $\text{H}_2\text{Se}(\text{g}) \xrightarrow{750 \text{ K}} \text{Se}(\text{l}) + \text{H}_2(\text{g})$

Other cycles may be possible that utilize  $\text{ZnSO}_4$  as an integral part of the process.

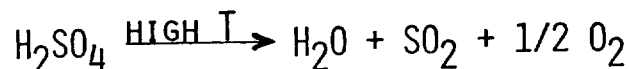
Decomposition of  $\text{ZnSO}_4$  can also be substituted as the high temperature step in place of decomposition of  $\text{H}_2\text{SO}_4$  vapor in thermochemical cycles such as those under development at the General Atomic Company (Norman, 1978) Westinghouse Electric Corporation (Farbman, 1978), and the Euratom Joint Research Centre at Ispra (van Velzen, 1978). The main reaction steps for these cycles are illustrated in Fig. 1. These cycles all produce about a 50-70 wt%  $\text{H}_2\text{SO}_4$  solution in

Fig. 1. Thermochemical cycles whose chemistry and closed loop operation have been verified in the laboratory.

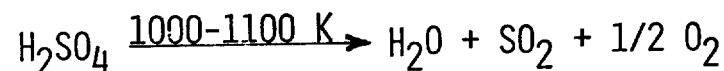
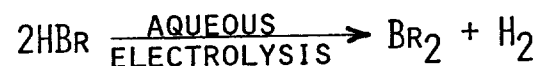
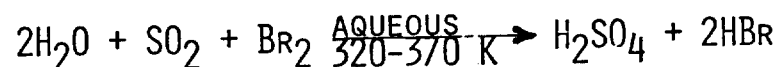
#### SULFUR-IODINE CYCLE



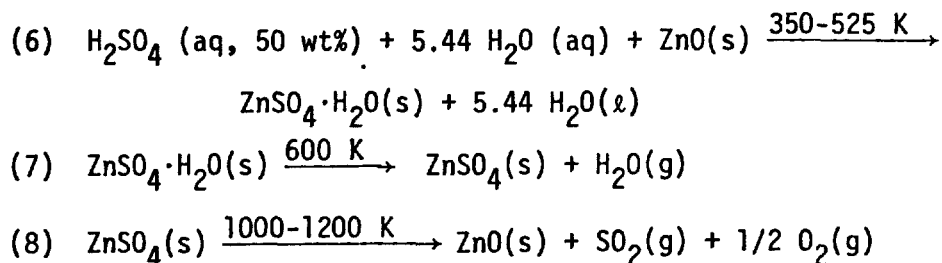
#### SULFUR CYCLE (PART ELECTROCHEMICAL)



#### SULFUR-BROMINE CYCLE (PART ELECTROCHEMICAL)



water that can be separated in relatively pure form from other reaction products. The sequence of reaction steps for conversion of  $\text{H}_2\text{SO}_4$  to  $\text{ZnSO}_4$  and the subsequent decomposition of  $\text{ZnSO}_4$  are shown below assuming a 50 wt%  $\text{H}_2\text{SO}_4$  feed material.



The sum of these reactions is equivalent to decomposing  $\text{H}_2\text{SO}_4$  directly. Part of the water, however, is separated out as liquid and avoids the use of heat for boiling. Some  $\text{SO}_3\text{(g)}$  (about 20% as much as  $\text{SO}_2$ ) will be present in the reaction (8) products, and will require separation and decomposition in another process step. The same situation prevails in the case of direct  $\text{H}_2\text{SO}_4$  decomposition.

Reaction (6) is an acid/base neutralization reaction that is exothermic by 83 kJ/mol, which is sufficient to heat the solution to ~450 K. By containing the reaction mixture in a pressure vessel and providing additional heat to attain 525 K, the  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  phase becomes highly insoluble, and can be precipitated out to provide a pure water product without the need for boiling. This rather unusual decrease in solubility of  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  with temperature is shown in Fig. 2

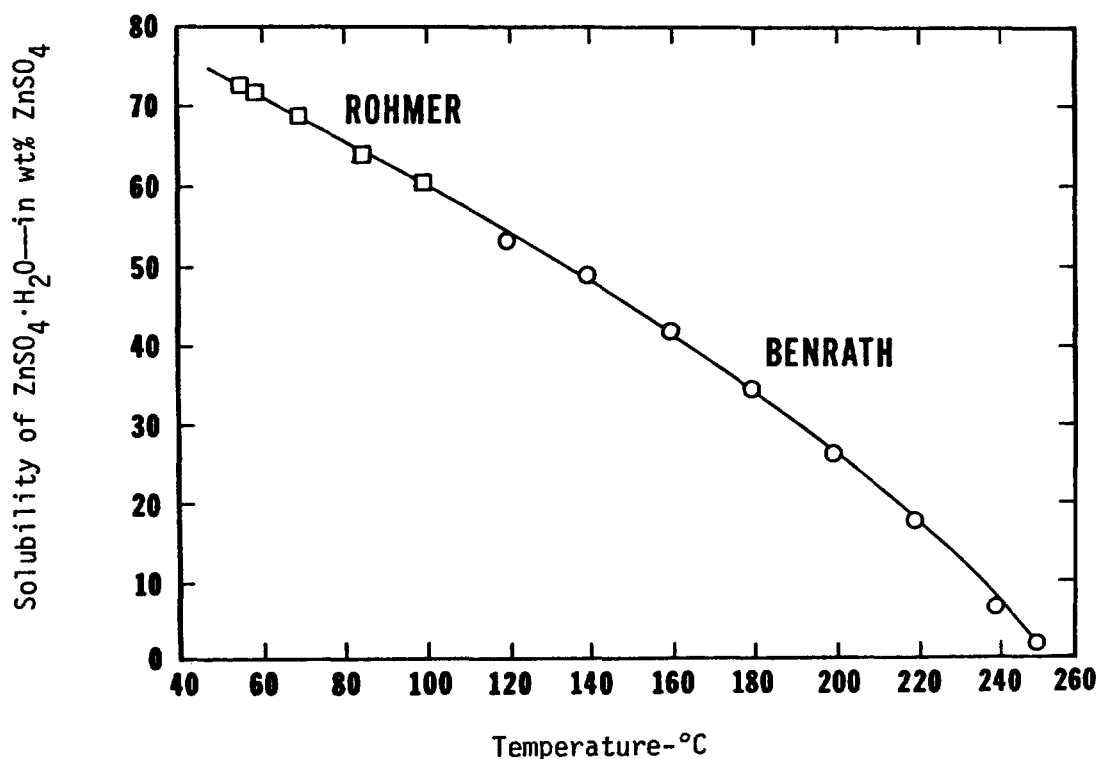
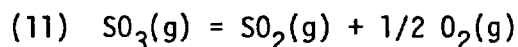
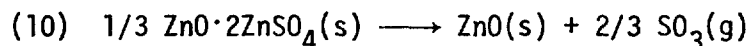
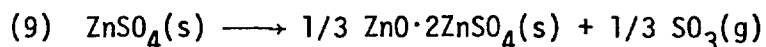


Fig. 2. Solubility of  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  drops to a low value at  $250^{\circ}\text{C}$ , thus permitting separation of the  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  phase from water without the need to expend energy for boiling.

(Rohmer, 1939; Benrath, 1941). Residual water remaining in the  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  precipitate needs to be evaporated and the hydrate needs to be decomposed according to reaction (7), with an enthalpy requirement of 80 kJ/mol. Steam generated by these drying and dehydration steps is at a sufficiently high temperature that it can be used for process heat elsewhere in the various thermochemical cycles.

Reaction (8) is the step that we are primarily concerned with in this work. The enthalpy requirement is quite high, 338 kJ/mol, for the reaction as written, and the kinetics of decomposition may be hindered depending upon various materials parameters and heating conditions. Although there is a substantial literature on  $\text{ZnSO}_4$  decomposition within our temperature regime of interest (e.g., Stern, 1966; Pechkovskii, 1957; Pechkovskii, 1958), the data appears to be complicated by heat and mass transport limitations as evidenced by a dependence on sample size and configuration. At lower temperatures, i.e., from 780-1000 K, the decomposition mechanism has been investigated by Hildenbrand and Lau (1979), who find that decomposition proceeds according to the following reactions:



Thus, at these lower temperatures the decomposition proceeds through an oxysulfate intermediate, and forms  $\text{SO}_3(g)$  as the initial gaseous product, even though at equilibrium under their conditions the  $\text{SO}_2/\text{SO}_3$  ratio would be about 15/1. The rate of conversion of  $\text{SO}_3$  to the equilibrium  $\text{SO}_3/\text{SO}_2/\text{O}_2$  mixture was found to be extremely slow unless catalysts were used at the temperatures of the study.

We anticipate that the decomposition mechanism for  $\text{ZnSO}_4$  may change substantially above about 1015 K, since at this temperature  $\text{ZnSO}_4$  undergoes a crystalline phase transformation from the low temperature alpha form, which is an orthorhombic  $\text{CuSO}_4$  type, to the high temperature beta form, which is a cubic high-cristobalite type (Spiess, 1978). Beta  $\text{ZnSO}_4$  is the only sulfate that is reported to have this type of structure. More importantly, the alpha to beta transformation is accompanied by a 28% volume expansion (Spiess, 1978) and an endothermic enthalpy change of 24 kJ/mol  $\text{ZnSO}_4$  (Hosmer, 1979). We would expect extensive shattering of the  $\text{ZnSO}_4$  crystallites in heatup through the alpha to beta transition, and the generation of fresh surfaces thus created may well influence the decomposition kinetics. We should further note that the transition enthalpy is extremely high, so that the rate of energy input will markedly effect the rate at which the transition takes place and hence the amount of thermal shock imposed on the crystallites. This study therefore was undertaken to make an initial assessment of the effects of heating rate through the alpha to beta transition in  $\text{ZnSO}_4$  on its decomposition kinetics.

#### EXPERIMENTAL

We heated the  $\text{ZnSO}_4$  specimens by radiant heating using four tungsten lamp ellipsoidal image furnaces, which were mounted horizontally in a square array and focussed simultaneously onto the surface of a given sample of  $\text{ZnSO}_4$  contained in a fused silica vial (see Fig. 3). In some of the runs, a layer of fine  $\text{Al}_2\text{O}_3$  powder, about 7 mm high, was first placed beneath the  $\text{ZnSO}_4$  to provide thermal insulation at that location. About 1.6 g of  $\text{ZnSO}_4$  were used in each run. The silica vial (1.5 cm i.d.) was attached to a mechanically pumped vacuum system, and a known ballast volume (1.0 l) was provided as an aid for PVT

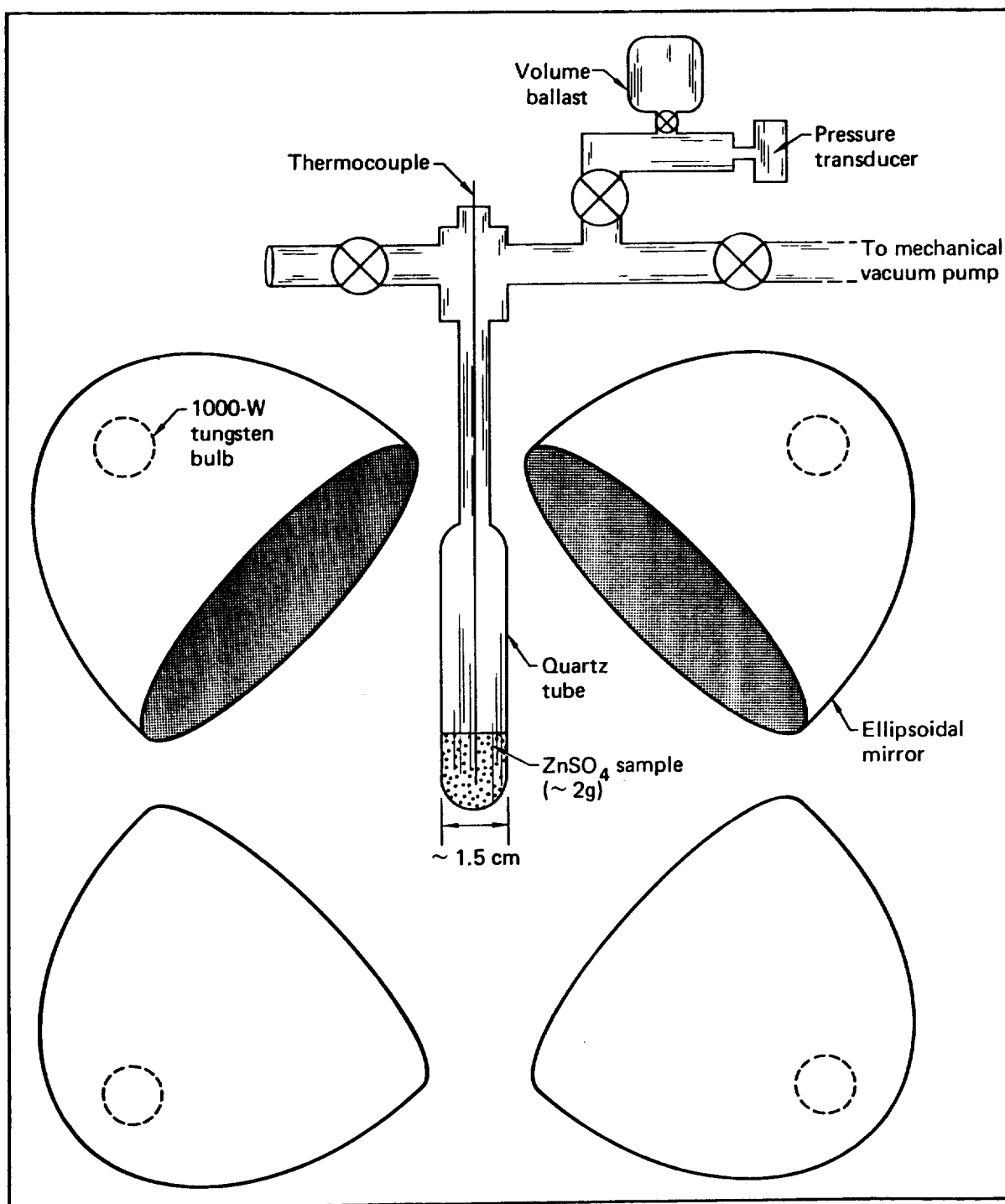


Fig. 3. Schematic of apparatus for examining the decomposition of  $\text{ZnSO}_4$ . Ellipsoidal mirrors focus the light from 1000-W bulbs onto a tube containing the sample and a thermocouple. This apparatus was used in a study to demonstrate that the decomposition rate depends on the heating rate through the  $\alpha$ -to- $\beta$  phase transition.

measurements of gas content. Pressures were measured with a capacitance manometer accurate to better than  $\pm 0.1\%$  over most of the range of 1-1000 torr. The uncertainty in measurement of moles of gas was limited to  $\pm 1\%$  however, because of the uncertainty in the average temperature of the gas in the measured volume. A Chromel-Alumel thermocouple, sheathed in stainless steel and surrounded by an open-ended  $\text{Al}_2\text{O}_3$  protection tube, was located in the center of the  $\text{ZnSO}_4$  sample, and was used to give an approximate value for the sample temperature. The four tungsten lamps had sufficient total power ( $\sim 4.0$  kW) to produce a temperature of 1200 K at the thermocouple location, and each image furnace gave an area of nearly uniform intensity of about  $1 \text{ cm}^2$ . We could observe the sample surface during a run through darkened glass windows.

To make a decomposition run, we started with a sample of reagent grade  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , and dehydrated it by heating to 500-650 K with the tungsten lamp furnaces set at a low power and with the sample under vacuum. We had to heat the sample slowly (4 hours to dehydrate) under these conditions to prevent spattering, and this produced an anhydrous product in the form of a fine freely-flowing powder. The sample and vial were weighed and then reheated and reweighed until a constant weight was attained. The material prepared in this manner could be exposed to air for only a few minutes before beginning to pick up water. However, we were able to make weighings quickly on a rapid read-out balance with a precision of  $\pm 0.01 \text{ g}$ . We also found that we could dehydrate more rapidly by using an overpressure of air to minimize spattering, e.g., one hour was sufficient to dehydrate under a 200 torr air overpressure, but the resultant product was caked, and upon shaking formed a coarse powder.

After dehydrating the  $\text{ZnSO}_4$  and determining its weight, we evacuated the system and isolated the sample vial and a section of the vacuum line (total volume =  $1.64 \text{ l}$ ) in a static vacuum, while maintaining sufficient furnace power to keep the sample at 650 K. The power was then increased at a controlled rate, taking care to assure that the image furnace was in proper focus and that each delivered the same amount of power during the heatup, until the final temperature of 1043 K was attained at the sample thermocouple. Our fastest heating rate was 2 minutes to go from 650 to 1043 K, and our slowest rate was 15 minutes for the same temperature interval. We followed the progression of the decomposition by measuring the total pressure of the evolved gases with the capacitance manometer, and calculated the moles of evolved gas using the ideal gas law. The balast volume ( $1.0 \text{ l}$ ) was used at the end of the experiment to provide an additional volume for checking the PVT relation. The total pressure of evolved gases in this system never exceeded 200 torr, so that condensation of  $\text{SO}_3(\text{g})$  was not a problem. After completion of the experiment, we determined the weight loss of the  $\text{ZnSO}_4$  as an additional measure of the total extent of decomposition.

## RESULTS

We will give a description here of two decomposition experiments that we conducted on fine  $\text{ZnSO}_4$  powder samples using heatup times of 2 and 15 minutes to attain 1043 K. The two samples are designated as sample A and sample B, respectively. Results of these experiments are summarized in Tables 1-3 and Fig. 4. We also made some additional runs at intermediate heatup times using both fine and coarse  $\text{ZnSO}_4$  powder samples. Experiments with the fine  $\text{ZnSO}_4$  powder at intermediate times confirmed the general type of behavior observed with samples A and B, but furnace conditions were not well controlled, and a further description is not warranted. We observed a different type of behavior with the coarse  $\text{ZnSO}_4$  powder, and that will be described.



#### Sample A - 2 Minute Heatup Rate

Sample A, for which we used the 2 minute heatup rate, was prepared by the technique previously described to give a fine freely-flowing powder with an insulating bed of  $\text{Al}_2\text{O}_3$  powder beneath it. The image furnaces were adjusted to illuminate the sides and top of the sample as uniformly as possible. Thus, with the combination of uniform illumination of the exposed surfaces and an insulating layer beneath the sample, we hoped to achieve a nearly isothermal sample condition. To initiate the run, sample A was heated from 650 to 1043 K in 2 minutes by applying 3.4 kW of power to the lamps. The power was held at that value when temperature was first attained, and then gradually decreased to 2.8 kW as the run progressed in order to maintain a reading of 1043 K at the sample center. We believe that a higher power requirement was needed during the early stages of decomposition because of an initial low absorptivity of the  $\text{ZnSO}_4$ . As the heating progressed, we noticed the development of an orange color in several regions of the sample surface, and the color tended to increase in area with time. With the appearance and increase in orange color, the absorptivity of the sample also increased, as evidenced by the fact that we were able to gradually reduce the power required to maintain the thermocouple reading at 1043 K.

After sample A had been at temperature for 60 minutes, we cooled it down and determined the weight loss up to that point. Upon cooling down, the orange color reverted back to white. We then again isolated the sample in a static vacuum, repeated the heatup schedule, and held the sample for an additional 35 minutes at 1043 K. Once at temperature, the sample regained the regions of orange color, and reestablished a continuation of its previous decomposition behavior. The sample became nearly all orange in color when decomposition was complete.

#### Sample B - 15 Minute Heatup Rate

The preparation of sample B was carried out in as identical a manner as possible to sample A. Heatup from 650 to 1043 K was started with 2.2 kW and continuously increased to 3.1 kW over the 15 minute heatup interval. The power then was gradually reduced as the decomposition progressed. Initially the decomposition rate was quite slow, amounting to only about 3% decomposition in 150 minutes, but at 150 minutes the decomposition rate accelerated in an autocatalytic manner. The same type of orange coloration was observed as in sample A when the autocatalytic reaction became established. Decomposition of sample B appeared to be complete in ~300 minutes based upon the evolved gas, and the run was terminated and the sample weighed after 350 minutes.

#### Coarse $\text{ZnSO}_4$ Powder

Heatup rate did not have as large an effect on the decomposition behavior of coarse  $\text{ZnSO}_4$  powder as on the fine freely-flowing material. Fig. 4 illustrates the typical behavior - namely a very slow, nearly linear decomposition rate. When a rapid heatup rate was used with the coarse powder, the initial decomposition rate was higher than for the fine material with the slow heatup rate, but the fine material passed up the coarse material when the autocatalytic effect set in. With a slow heatup rate for the coarse powder, the initial decomposition rate was similar to the slow heatup fine material, and again continued in a nearly linear manner with time.

#### Decomposition Results - Samples A and B

According to the observed weight loss behavior (see Table 1), sample A had decomposed by 82% after 60 minutes, and by an additional 19% after the second heating of 35 minutes. Thus, within the precision of the measurements, it was completely

TABLE 1 Weight Loss of ZnSO<sub>4</sub> Samples upon Heating to 1043 K, and Calculated Percent Decomposition of ZnSO<sub>4</sub> Based upon ZnSO<sub>4</sub> Loss

Sample	Sample Heatup Time	Time at Temp.	Initial Wt. ZnSO <sub>4</sub>	Initial Moles ZnSO <sub>4</sub>	Wt. Loss During Heating	Moles SO <sub>3</sub> Lost	% ZnSO <sub>4</sub> Decomp.
A	2 min.	60 min.	1.58 g	0.0098	0.64 g	0.0080	82%
A	(reheat)	35 min.	-	-	0.15 g	0.0019	19%
B	15 min.	350 min.	1.60 g	0.0099	0.78 g	0.0097	98%

TABLE 2 Calculated Equilibrium Gas Composition at the End of Each ZnSO<sub>4</sub> Decomposition Run at 1043 K

For the Reaction  $\text{SO}_3(\text{g}) = \text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$ ,

$$K_{\text{equil.}} = 0.945 \text{ atm}^{1/2} \text{ at } 1043 \text{ K}$$

System Volume = 1.64 L

Average System Temperature = 305 K

Sample	Sample Heatup Time	Final System Pressure	Total Moles of Gas	Calc. Moles SO <sub>3</sub>	Calc. Moles SO <sub>2</sub>	Calc. Moles O <sub>2</sub>	Calc. Moles SO <sub>3</sub> +SO <sub>2</sub>	% ZnSO <sub>4</sub> Decomp.
A	2 min.	129 torr	0.0111	0.0015	0.0064	0.0032	0.0079	81%
A	(reheat)	26 torr	0.0023	0.0002	0.0014	0.0007	0.0016	16%
B	15 min.	161 torr	0.0139	0.0021	0.0079	0.0039	0.0100	101%

TABLE 3 Summary of Times Required to Attain Various Degrees of Decomposition of ZnSO<sub>4</sub> at 1043 K

Sample	Sample Heatup Time	Amount ZnSO <sub>4</sub> Decomposed at 1043 K			
		10%	33.3%	50%	90%
A	2 min.	5 min.	9 min.	14 min.	67 min.
B	15 min.	15 min.	173 min.	187 min.	284 min.

converted to ZnO after the second heating. For sample B, the weight loss data indicated 98% decomposition after 350 minutes of heating, which within the precision of the data is essentially complete decomposition.

The gas generation data (see Table 2 and Fig. 4), indicated a pressure of 129 torr for sample A after 60 minutes of heating, which, based on a system volume of 1.64 L and an average system temperature of 305 K, gives 11.1 mmoles of gas. From the literature data (Stern, 1966) on the SO<sub>3</sub>/SO<sub>2</sub>/O<sub>2</sub> equilibrium, we can calculate the corresponding amounts of the constituent gaseous species assuming an equilibration temperature of 1043 K (see Table 2), and obtain 1.5 mmoles SO<sub>3</sub>, 6.4 mmoles SO<sub>2</sub>, and 3.2 mmoles O<sub>2</sub>. This further gives a total of 7.9 mmoles for the sum of

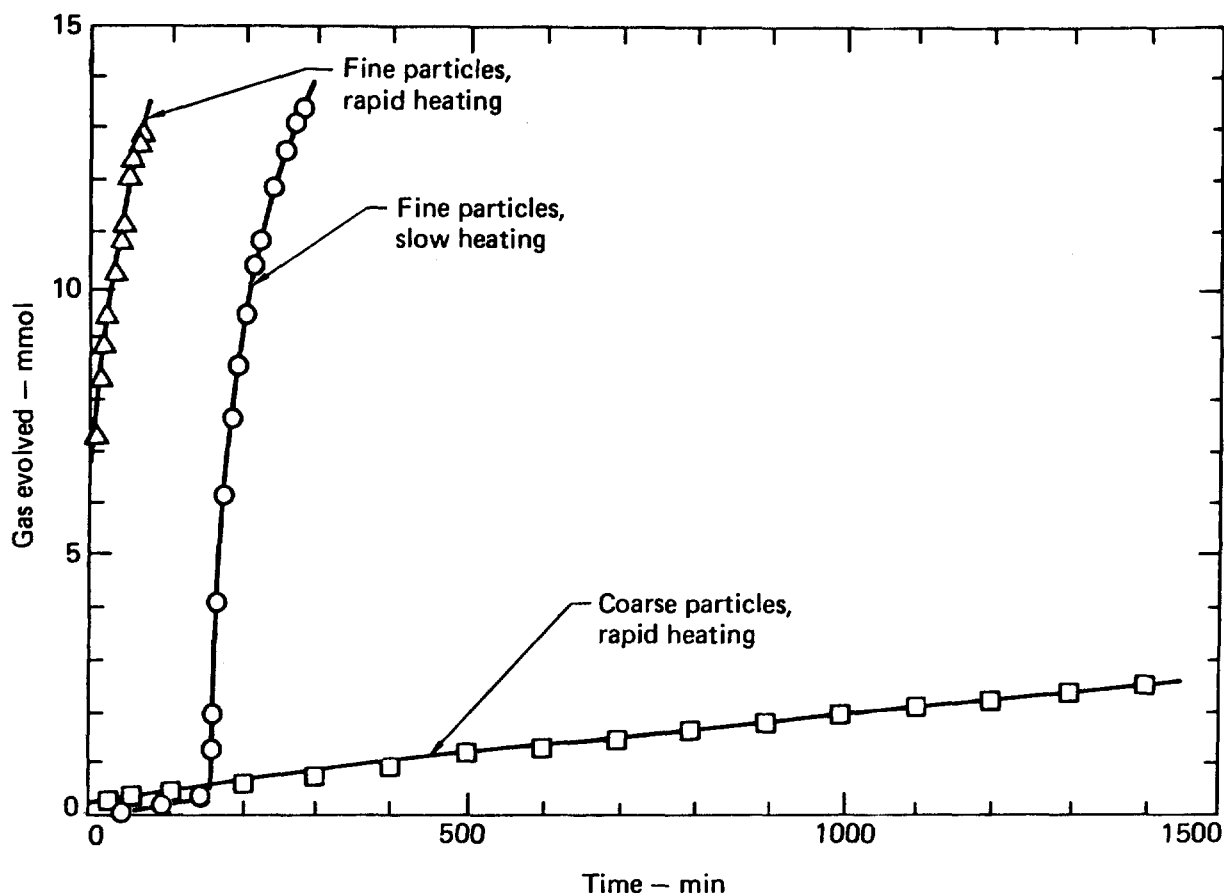


Fig. 4. Effect of heating rate and particle size on decomposition rate of  $\text{ZnSO}_4$ . A greater heating rate causes a greater decomposition rate for fine particles of  $\text{ZnSO}_4$ ; coarse particles of  $\text{ZnSO}_4$  decomposed slowly even when heated rapidly. These are preliminary results of our program to study  $\text{ZnSO}_4$  decomposition and indicate that a rapid heating rate through the  $\alpha$ -to- $\beta$  phase transition fractures the particles of  $\text{ZnSO}_4$ , causing more rapid decomposition. Complete decomposition to  $\text{ZnO}$  should produce about 13 mmol of evolved gases.

the sulfur containing species, which compared with the original 9.8 mmoles of  $\text{ZnSO}_4$  (see Table 1) corresponds to 81% decomposition, in essential agreement with the weight loss results. Similarly, we obtain an additional 1.6 mmoles of sulfur containing species for 16% decomposition during the second heating of sample A. For sample B, the same type of analysis gives 101% decomposition at the end of the run. Thus, the gas evolution experiments are in agreement with the weight loss results on decomposition, provided that we assume that equilibrium has been established for the product gases at  $\sim 1043$  K.

If we assume further, that the  $\text{SO}_3/\text{SO}_2/\text{O}_2$  equilibrium is established instantaneously as decomposition proceeds, we can use the gas generation data as a measure of the decomposition behavior of  $\text{ZnSO}_4$  over the entire decomposition range. This may be a tenuous assumption under conditions of rapid decomposition of  $\text{ZnSO}_4$  when insufficient time is available for equilibration. Nonetheless, we have used this basis to estimate the times required to attain various degrees of decomposition for samples A and B (see Table 3).

## DISCUSSION

As a preface to the discussion of this work, we would like to point out that in dynamic experiments of the type conducted here, it is very difficult to provide accurate instrumentation and to maintain precise experimental control. Our work is therefore semi-quantitative in nature, but suffices for the comparative type of experiments in this study. Conclusions that we can draw from this work are the following:

- A rapid heatup rate of fine  $\text{ZnSO}_4$  particulates through the  $\alpha$ - $\beta$  phase transition significantly accelerates its subsequent decomposition behavior.
- An auto-catalytic process occurs during the decomposition of fine  $\text{ZnSO}_4$  particulates at  $\sim 1043$  K for either rapid or slow heatup times after a few percent decomposition has taken place.
- The gaseous products ( $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{O}_2$ ) from the decomposition of fine  $\text{ZnSO}_4$  particulates at  $\sim 1043$  K were found to be at or near equilibrium in these experiments.

The decomposition behavior of  $\text{ZnSO}_4$  is more complex than we had anticipated earlier based on a simple particle fracturing approach for the  $\alpha$ - $\beta$  transition. The auto-catalytic behavior that we found for sample B is especially puzzling, and some speculation seems worthwhile. A possible explanation may be the following. When sufficient decomposition occurs to produce  $\text{ZnO}$  on the particle surfaces exposed to the radiant beam, there is a localized temperature increase in the  $\text{ZnO}$  due to its high absorptivity as compared with the  $\text{ZnSO}_4$  and  $\text{ZnO} \cdot 2\text{ZnSO}_4$  phases. Heat would now be conducted more efficiently to particles containing  $\text{ZnO}$ , as well as to the immediately surrounding particles, to accelerate their decomposition. The development of the orange color as decomposition progresses, we believe, is due to the  $\text{ZnO}$  phase, and would account for its high absorptivity. Although such a  $\text{ZnO}$  hot spot effect would explain an enhanced rate of decomposition, we do not think that it accounts entirely for the observed autocatalytic behavior. The observation of gaseous equilibrium for  $\text{SO}_3/\text{SO}_2/\text{O}_2$  in this work suggests that surface catalysis may be present, and may be an important contribution to the autocatalytic effect. Hildenbrand and Lau (1979), in studying the decomposition mechanisms of a number of sulfates, have found that  $\text{SO}_3(\text{g})$  is generally the initial species evolved during decomposition, and that catalytic conversion of  $\text{SO}_3(\text{g})$  to  $\text{SO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is necessary to enhance the decomposition rate. Otherwise, localized buildup of  $\text{SO}_3(\text{g})$  can significantly retard or even stop the decomposition process if it reaches the saturation pressure. We believe that  $\text{ZnO}$  is probably an effective catalyst under our experimental conditions. Neither  $\text{ZnSO}_4$  or  $\text{ZnO} \cdot 2\text{ZnSO}_4$  are likely catalysts, since in sample B they should both have been present during the initial  $\sim 150$  minutes at  $1043$  K, yet autocatalysis did not occur until then. Auto-catalysis probably set in at that point because the  $\text{ZnO}$  phase first began to appear on some of the particle surfaces.

We would like to compare more quantitatively the autocatalytic decomposition region in sample B with the decomposition behavior of sample A, since the two curves appear to be very similar (see Fig. 4). A more quantitative comparison (see Table 3), shows that sample A is indeed decomposing more rapidly than sample B in the autocatalytic region. For example, the time required for sample A to go from 10-50% decomposition is 9 minutes compared to 28 minutes for sample B. We believe that this is a manifestation of the greater degree of fracturing in sample A as compared to sample B.

It is also significant to note that the process of cooling down sample A after 60 minutes of heating, exposing it to air while weighing, and repeating the heatup

procedure, did not affect its decomposition behavior; i.e., it continued along the same decomposition curve. Thus, cycling of the  $\text{ZnSO}_4$  as above, including an exposure to air, does not seem to adversely affect such factors as surface condition or catalytic behavior of the partially decomposed  $\text{ZnSO}_4$ .

Finally, we need to point out that the gas pressures generated by samples A and B exceeded the equilibrium decomposition pressures reported in the literature (Ingraham, 1963) for 1043 K. The highest pressure that we obtained was 161 torr for sample B (see Table 2). From the literature we find a total pressure of only 24 torr for decomposition of  $\text{ZnO} \cdot 2\text{ZnSO}_4$  at 1043 K. A temperature of 1130 K is required to attain a pressure of 161 torr. Hence, our actual sample temperature must have been at least 87 K higher than indicated by the thermocouple. This is not too surprising since we could visually observe hot spots on the sample surfaces. Also, the thermocouple position is expected to be in the coldest region of the samples and therefore is a minimum reading. We do not think that the error in sample temperature was much greater than 87 K, since the samples were insulated on the bottom and fairly uniformly illuminated on the exposed surfaces. Nor, does an error in temperature of this magnitude change our conclusions which are mainly comparative in nature. There is a slight shift to greater decomposition of  $\text{SO}_3$  to  $\text{SO}_2$  and  $\text{O}_2$ , but this is not significant within the accuracy of our measurements.

### CONCLUSIONS

We have found that a rapid heatup (650-1043 K in 2 min.) of  $\text{ZnSO}_4$  through its  $\alpha$ - $\beta$  transition at 1015 K significantly accelerates its subsequent rate of decomposition to solid  $\text{ZnO}$  and gaseous  $\text{SO}_3$ ,  $\text{SO}_2$  and  $\text{O}_2$ . We believe this occurs primarily because of a large volume increase (28%) in the  $\alpha$ - $\beta$  transition that causes fracturing of  $\text{ZnSO}_4$  particulates and creates a high surface area for gas release. The situation is more complex than this, however, and we have found that an autocatalytic process occurs, even when  $\text{ZnSO}_4$  is heated up more slowly. We interpret this to mean that  $\text{ZnO}$  is a surface catalyst that promotes equilibration of the gaseous products and as a consequence further accelerates the decomposition rate.

### ACKNOWLEDGEMENT

We would like to express our appreciation to Mr. William H. Parrish for design and construction of the apparatus used in this study.

### REFERENCES

- Benrath, A. (1941). About the solubility of salts and salt mixtures in water at temperatures above 100°C. III. Z. anorg. Chem., **247**, 147-160.
- Farbman, G. H. (1978). The Westinghouse Sulfur Cycle hydrogen production process: program status. In T. N. Veziroglu and W. Seifritz (Ed.), Hydrogen Energy System, Proceedings of the 2nd World Hydrogen Energy Conference, Zurich, Switzerland, 21-24 August 1978, Vol. 5, Pergamon Press, Oxford. pp. 2485-2504.
- Hildenbrand, D. L., and Lau, K. H. (1979). High temperature chemistry of hydrogen production cycles. Stanford Research Institute, Menlo Park, CA 94025. private communication.
- Hosmer, P. K. (1979). Measurement of the high temperature enthalpies of  $\text{ZnSO}_4$  and  $\text{ZnO} \cdot 2\text{ZnSO}_4$  by drop calorimetry. Lawrence Livermore National Laboratory, Livermore, CA 94550. private communication.
- Ingraham, T. R., and Kellogg, H. H. (1963). Thermodynamic properties of zinc sulfate, zinc basic sulfate, and the system  $\text{Zn-S-O}$ . Trans. Met. Soc. AIME, **227**, 1419-1426.
- Krikorian, O. H. (1978). The  $\text{ZnSe}$  thermochemical cycle for hydrogen production: chemical and process design studies. In T.N. Veziroglu and W. Seifritz (Ed.),

- Hydrogen Energy System, Proceedings of the 2nd World Hydrogen Energy Conference, Zurich Switzerland, 21-24 August 1978, Vol. 2, Pergamon Press, Oxford. pp. 791-807.
- Norman, J. H., Mysels, K. J., O'Keefe, D. R., Stowell, S. A., and Williamson, D. G. (1978). Chemical studies of the General Atomic Sulfur-Iodine Thermochemical Water-Splitting Cycle. In T. N. Veziroglu and W. Seifritz (Ed.), Hydrogen Energy System, Proceedings of the 2nd World Hydrogen Energy Conference, Zurich, Switzerland, 21-24 August 1978, Vol. 2, Pergamon Press, Oxford. pp. 513-543.
- Pechkovskii, V. V. (1957). Thermochemical decomposition of zinc sulfate. J. Inorgan. Chem. USSR, 11, 1467-1470.
- Pechkovskii, V. V. (1958). Decomposition of zinc and cobalt sulfates in current of sulfur dioxide and air. J. Appl. Chem. USSR (English Translation), 31, 1130-1133.
- Rohmer, R. (1940). Dehydration by wet way of zinc sulfate heptahydrate. Solubility curve of the hydrates. Compt. Rend., 210, 669-674.
- Spiess, M., and Gruehn, R. (1978).  $\text{H-ZnSO}_4$ , the first sulfate with a cubic h-cristobalite structure. Naturwissenschaften, 65, 594.
- Stern, K. H., and Weise, E. L. (1966). High Temperature Properties and Decomposition of Inorganic Salts. Part 1. Sulfates. National Standard Reference Data Series--National Bureau of Standards 7. U.S. Government Printing Office, Washington, D. C. pp. 34-35.
- van Velzen, D., Langenkamp, H., Schütz, G., Lalonde, D., Flamm, J., and Fiebelmann, P. (1978). Development, design and operation of a continuous laboratory-scale plant for hydrogen production by the Mark-13 Cycle. In T. N. Veziroglu and W. Seifritz (Ed.), Hydrogen Energy System, Proceedings of the 2nd World Hydrogen Energy Conference, Zurich, Switzerland, 21-24 August 1978, Vol. 2, Pergamon Press, Oxford. pp. 649-665.